THE EFFECT OF DIFFERENT SiO_2/Al_2O_3 RATIOS OF HZSM-5 ON THE CONVERSION OF PALM OIL TO LIQUID FUELS

Nor Aishah Saidina Amin and Farizul Hafiz Kasim
Chemical Reaction Engineering Group (CREG),
Faculty of Chemical And Natural Resources Engineering,Universiti Teknologi Malaysia, 81310 Sekudai, Johor.
Fax: 607-5581463 Tel: 607-5505338 Email: noraishah@fkkksa.utm.my

ABSTRACT

Palm oil can be converted to liquid fuels by catalytic cracking process. The present effort studies the conversion of palm oil vapors to liquid hydrocarbon fuels over HZSM-5 zeolite catalysts with different SiO_2/Al_2O_3 ratios. The direct synthesis of HZSM-5 zeolite with SiO_2/Al_2O_3 ratios is reported in this paper. The characterization of the catalyst is performed using X-Ray diffraction (XRD) and Fourier transform infrared (FTIR). The catalyst activity test is conducted in a micro-packed bed reactor via a continuous system mode. The catalyst is loaded in the middle of the reactor and supported with glass wool. Nitrogen gas is used to flush the system before and after the experiment. The products were analyzed using gas chromatograph. From the experimental result, the conversion of palm oil over HZSM-5 with SiO_2/ Al_2O_3 = 30 demonstrated a high percentage of gasoline compared to the other samples.

Keywords: Palm Oil, Liquid Fuels, HZSM-5, SiO_2/Al_2O_3 Ratio, Catalytic Conversion.

INTRODUCTION

The utilization of vegetable oils triglycerides of long chain fatty acids and glycerols as the source is promising. The use of vegetable oils as raw material for catalytic cracking process to obtain gasoline and other chemicals has recently attracted attention (Haag and Rodewald, 1980, Prasad and Bakhshi, 1986a, 1986b, Idem et. al., 1997, Bhatia et. al., 1998). Various kind of vegetable oils were reported to successfully formed gasoline and other useful chemicals after the catalytic conversion process. Studies conducted by researcher at Mobil (Haag et al.), showed that vegetable oils such as castor, corn, jojoba and palm oil could be converted to clean premium transportation fuels and useful chemicals. Work by Prasad et. al., (1986a) observed 60 to 95 wt% conversion level of canola oil to gasoline, containing 60-70 wt% aromatic hydrocarbon. Prasad at. al., (1986b) then continued their work by adding steam in the feed stream with canola oil. The liquid hydrocarbon products contained less aromatics compounds.

HZSM-5 catalyst is found to be the best cracking catalyst in terms of conversion and aromatics productions (Bhatia et al., 1998). The characteristics of the catalyst also affect the production of gasoline (Prasad et al., 1986). The acidity of the catalyst is found to be one of the most important factors in the cracking process whereby the conversion is found to decrease with the decrease in acidic strength (Bhatia, 1990).

Cracking can only proceed on the relatively strong acid sites (Groenenboom, 1989). The acidity of the catalyst, especially HZSM-5, is found to be related to their silica alumina ratio. Topsoe et al. (1981), Chu and Chang (1985) and Segawa et al. (1988) postulated that the acidity depend on the aluminium ions in the zeolite framework. The acidic strength of the zeolite increase when there is more aluminium in the framework. The acid density will be affected by the change in SiO_2/Al_2O_3 and therefore affecting the amount of the liquid fuel obtained. The objective of this work is to investigate the effect of SiO_2/Al_2O_3 in HZSM-5 to the palm oil to gasoline process.

EXPERIMENTAL

Feed Material

The feed was a refined, bleached and deodorized (RBD) commercial grade palm oil 'Vesawit' that was purchased from the local market.

Catalyst Preparation

HZSM-5 was prepared via direct synthesis following the procedure by Plank et al. (1974) with a slight modification by Sharif (1999). Firstly, NaZSM-5 was prepared by mixing SiO_2 into tetrapropyl

ammonium bromide (TPABr) solution. The dissolved SiO_2 then was mixed with aluminum sulfate, $Al_2(SO_4)_3.16H_2O$ solution. The mixing was placed in an autoclave non-stirred pressure vessel.

Three solutions, namely solution A (contained $Al_2(SO_4)_3.16H_2O$, TPABr, H_2SO_4 and distilled water) solution B (contained $NaSiO_3$ and distilled water) and solution C (contained NaCl and distilled water) were prepared. Solution C was put in the autoclave non-stirred pressure vessel and then was stirred by Heidolph RZR-2000 stirrer. Then solution A and solution B was slowly poured into solution C simultaneously. The white slurry product then will be stirred for 15 hours. Finally, the autoclave was sealed and put into the oven for seven days at 170°C.

After seven days, the zeolite was washed and filtered. The procedure was repeated three times to remove any contaminants from the zeolite. The zeolite then was dried in the oven for 15 hours at 100°C. After the drying process, the zeolite was calcined in the furnace at 550°C for five hours. The purpose of putting the zeolite in the furnace was to oxidize the organic cation and impurities.

The zeolite that was obtained from the experiment is actually NaZSM-5. The conversion of NaZSM-5 to HZSM-5 was carried out by the ion-exchange method was employed. 1g NaZSM-5 was dissolved in 25ml NH_4NO_3 aqueous, stirred and refluxed for six hours at 80°C. This step was repeated three times. The HZSM-5 then once again was filtered, washed and dried at 100°C. The HZSM-5 was calcined again at 550°C for five hours. The catalysts were labeled as HZSM-5 (30), HZSM-5 (50) and HZSM-5 (70) in accordance to its SiO_2/Al_2O_3.

Experimental Set-Up and Procedure

The catalytic conversion of palm oil to gasoline over modified HZSM-5 zeolite as a catalyst was carried out in a small-scale continuous downward flow fixed-bed reactor. The refined, bleached and deodorized palm oil as raw material was injected to the system with a syringe pump. The palm oil then was heated to the operation temperature using a furnace. The reactor was a stainless steel tube with 9 mm I.D. and 30 cm length. The catalyst was supported on a glass wool.

The rig was assembled on 75 cm (L) X 52 cm (W) X 152 cm (H) frame structure. The frame structure was made from dexion-type mild steel angle bar. ¼ in. stainless-steel tube was employed as the tubing system of the rig. The schematic diagram of the experiment rig is shown in Figure 1

Gas chromatography was used to analyze the liquid products. SGE 100-meter column was used to separate the components of the products. For each experiment, products identified were lumped under several chemical groups, depending on their retention times. These included C_5-C_{11} range hydrocarbons, which were categorized as gasoline range hydrocarbons, C_{12}-C_{15} range hydrocarbons and heavy hydrocarbons. Other Organic Products (OOP) represents the peaks that cannot be identified. The retention time of the peaks in this range was before the C_5 retention time.

RESULTS AND DISCUSSION

Catalyst Characterization

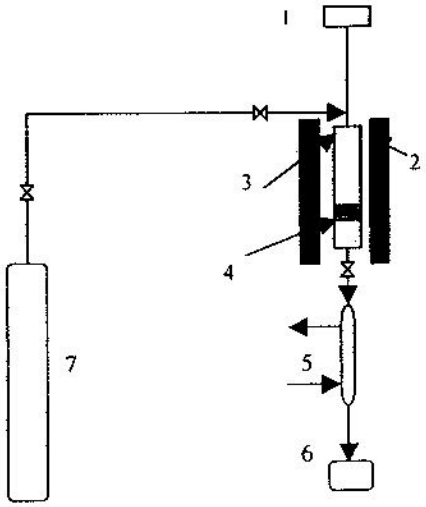
X-ray diffraction (XRD) was used to analyze the structural identification and determination of the relative crystallinity, RC of the synthesis HZSM-5 (assuming that the commercial HZSM-5 is 100% crystalline). The determination of the RC was based on the area of characteristic peaks in the 2θ range of 22.5 – 25.0°.

Figure 2(a) shows the diffractogram of HZSM-5 (30), HZSM-5 (50) and HZSM-5 (70), while figure 2(b) shows the commercial HZSM-5. It shown that all the HZSM-5 have almost the same diffractogram pattern. The comparison between HZSM-5 (30), HZSM-5 (50) and HZSM-5 (70) with commercial HZSM-5 indicates that the catalysts are undoubtedly in HZSM-5 family.

Table 1 shows the crystallinity percent of the synthesis HZSM-5 compared to the standard HZSM-5. The HZSM-5 (30) has the highest crystallinity followed with HZSM-5 (50) and HZSM-5 (70). The difference between the crystallinity was due to the different composition of chemicals when the catalyst was synthesized. The decreased of RC value of HZSM-5 indicated the HZSM-5 structure in those samples collapsed (Van Mao et. al., 1999).

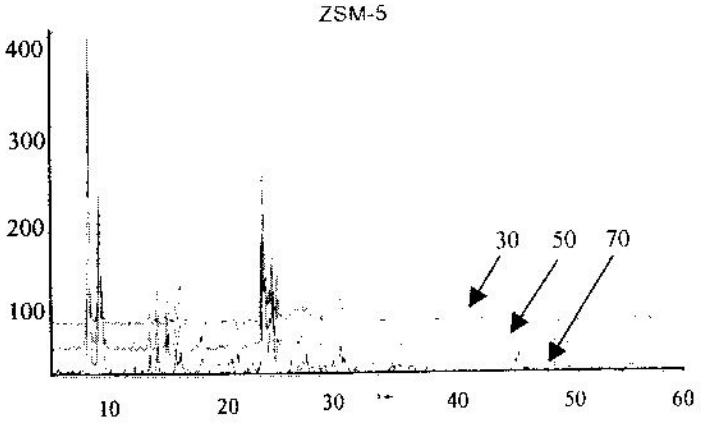
Catalyst Performance

Organic liquid products were produced with HZSM-5 (30) and HZSM-5 (50) as the catalysts. The HZSM-5 (70), however did not produce any liquid product because the acidic strength of the catalyst was not strong enough to crack the unsaturated double bonds of olein in the palm oil. Therefore, the double bonds formed the more stable saturated single bond stearin. The stearin exists in liquid phase at temperatures above 40°C and in solid phase at room temperature. The RC of HZSM-5 (30), HZSM-5 (50) and HZSM-5 (70) are 68.9%, 53.6% and 46.8% respectively. The RC decreased with higher SiO_2/Al_2O_3 ratios.

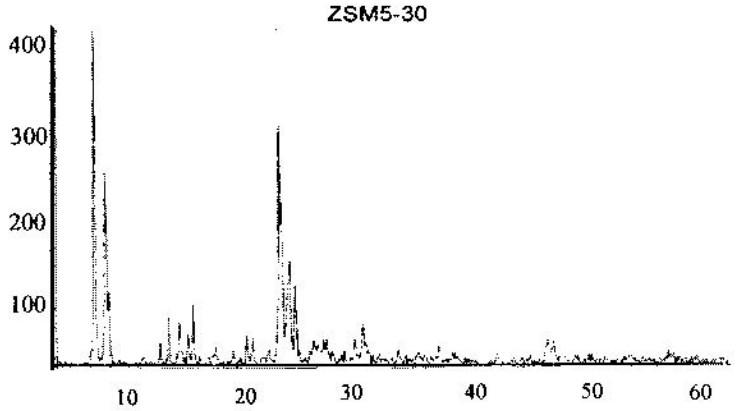


1. Syringe Pump; 2. Furnace
3. Reactor; 4. Catalyst;
5. Condenser; 6. Liquid Collector;
7. Nitrogen Gas

Figure. 1. Schematic diagram of the experiment rig



2(a)



2(b)

Fig. 2. Diffractogram of (a) HZSM-5 (30), HZSM-5 (50) and HZSM-5 (70) and (b) Commercial HZSM-5

Table 1: Relative crystallinity values of the synthesis HZSM-5 compared with the commercial HZSM-5

SiO_2/ Al2O_3	Relative Crystallinity (RC)
Commercial HZSM-5	100
30	68.9
50	53.6
70	46.8

The results in Figure 3 indicate the weight percent of the hydrocarbons ranging from OOP to heavy hydrocarbons for sample with 30 and 50 SiO_2/ Al_2O_3 ratios. 49% of gasoline was produced for the HZSM-5 (30) sample compared to just 37% for the HZSM-5 (50) sample.

Both catalysts samples gave an almost similar range of C_{12}-C_{15} hydrocarbons while hydrocarbons >C_{15} were observed for catalyst sample with SiO_2/ Al_2O_3 = 50. The wt % of OOP for HZSM-5 (30) and HZSM-5 (50) were 20% and 32% respectively.

The results in Figure 3 could be attributed to the acidic strength of the zeolite catalyst. The cracking activity is related to the acidic strength of the zeolite (Groenenboom, 1989). In free metal zeolite, the decrease of the concentration of acid sites parallels with the increasing of SiO_2/ Al_2O_3 ratio (Ivanov et. al., 1999). Therefore, because the HZSM-5 (30) had strong concentration of acid sites than HZSM-5 (50), it could cleave the long chain of palm oil and formed a gasoline range hydrocarbons efficiently.

For the HZSM-5 (50) sample, the lower active acid sites concentration means the cracking of the longer chains of triglycerides are not easily carried out. Moreover, the crystallinity of the HZSM-5 is low, suggesting the pores of the zeolite is not properly formed. This affected the residence time of the reactant vapor to reform in the pores.

The crystallinity of the HZSM-5 (30) catalyst is also contributed to the lower percentage of gasoline products. Since the pores are not properly intact the cracking could not be effectively carried out.

For the case of OOP, HZSM-5 (30) give a slightly lower percentage then HZSM-5 (30). The acidic strength of HZSM-5 (30) probably provided a condition for oligomerization of the smaller chains of hydrocarbons to form gasoline.

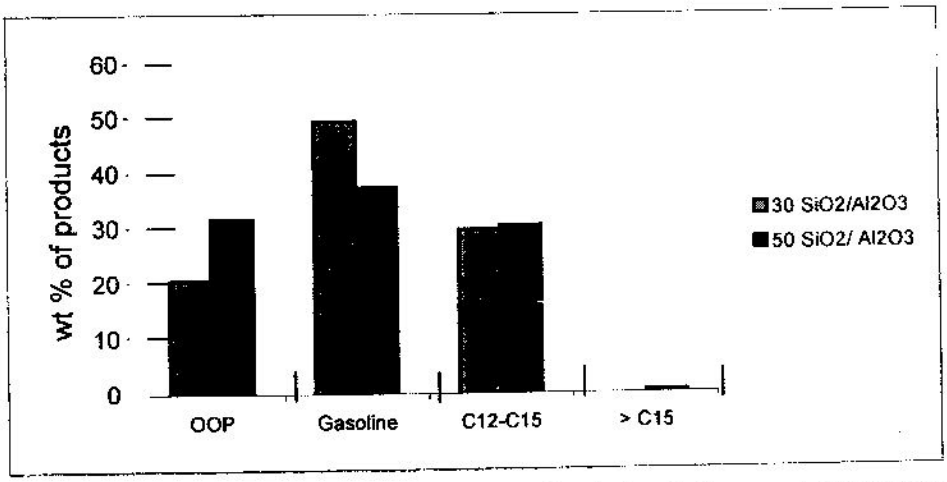


Figure 3: Weight percentage of OOP, Gasoline, C_{12}-C_{15}, and > C_{15} obtained in the experiments with 30, SiO_2/ Al_2O_3 HZSM-5

The OOP exist in the products, were believed to be aromatics products. Idem et al., (1996) in his work on catalytic conversion of canola oil found that HZSM-5 can give high yields of organic liquid products and aromatic hydrocarbon. Bhatia et al. (1998), also obtained benzene, toulene and xylene in his work on catalytic conversion of palm oil over potassium impregnated HZSM-5.

Besides the acidity of those catalysts, the shape selectivity of HZSM-5 also had a function for the formation of hydrocarbon. This explains why HZSM-5 (70) and HZSM-5 (50) zeolite catalysts with collapsed structure worse than HZSM-5 (30) produced less gasoline range product. HZSM-5 is a shape selective catalyst, which only let the small hydrocarbons range products to diffuse through the interconnecting pores.

CONCLUSIONST

The acidic strength of HZSM-5 zeolite is affected by the SiO_2/ Al_2O_3 ratios in the framework. The acidic strength of the sample facilitates the cracking activity of larger chain hydrocarbons. With the interconnecting pores of the HZSM-5 zeolite, the catalyst is a promising catalyst to produce gasoline because of its shape selective ability. However, the function of the catalyst in the cracking of longer hydrocarbons to gasoline is to balance cracking and oligomerization reactions which is affected by the acidic density of the catalyst active sites.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Ministry of Science, Technology and the Environment, Malaysia for funding the project under IRPA grant Vot. No. 72341.

REFERENCES

Bhatia, S., (1990). Zeolite Catalysis Principles and Applications. CRC Press, Inc., Boca Raton, Florida, USA

Bhatia S., H. J. Kee, L. M. Lan and A. R. Mohamed (1998). Production of Bio-Fuel by Catalytic Cracking of Palm Oil: Performance of Different Catalyst. Proc. of the Biofuel, PORIM intl. Biofuel and Lubricant Conf: 107-112

Bhatia. S., Noor Asmawati M. Z and Farouq T. (1998) Catalytic Conversion of Palm Oil over Potassium Impregnated HZSM-5 Catalyst and Hybrid Catalyst: Gasoline Production

C. J. Groenenboom, (1989). Zeolite and Matrix Structures and Their Role in Catalytic Cracking. Zeolite as Catalyst, Sorbents and Detergen Builders, 99-113

Chu, C. T-W. and Chang, C. D. (1985) Isomorphous Substitution in Zeolite Frameworks. 1. Acidity of Surface Hydroxyls in $[B]^-$, $[Fe]^-$, $[Ga]^-$, and $[Al]^-$ ZSM-5. The J. of Phy. Chem. 89; 1569-1571

Haag, W.O., Rodewald, P. G. and Weisz P. G. (1980). Catalytic Production of Aromatics and Olefin from Plant Materials. 180 A. C. S. National Meet.

Idem R. O., S. P. R. Katikaneni, N. N. Bakhshi. (1997) Catalytic Conversion of Canola Oil to Fuels and Chemicals: Roles of Catalyst Acidity, Basicity and Shape Selective on Product Distribution. Fuel Pro. Tech. 51. 101-125.

Ivanov, A.V., Graham, G. W. and Shelef, M. (1999). Adsorption of Hydrocarbons by ZSM-5 Zeolites With Different SiO_2/ Al_2O_3 Ratios: A Combined FTIR and Gravimetric Study. App. Cat. B: Env. 21. 243-258

Plank C.J., Rosinski, E. J. and Hawthow, W. P. (1964). Acid Crsytalline Aluminosilicates, 165, IEC Prod. Res. Dev

Segawa, K., Sakaguchi, M. and Kurusu, Y. (1988). Investigation of Acidic Properties of H-Zeolites as a Function of Si/ Al ratio.In: Bibby, D. M., Chang. C. D., Howe, R.F. and Yurchak, S. Methane Vonversion. Amsterdam: Elsevier Science Publishers B.V; 579-588

Sharif Hussein S. Z. (1999). Synthesis, Characterization and Catalytic Testing of Modified HZSM-5 Catalyst for Single Step Conversion of Methane to Gasoline. M. Eng Thesis. UTM

Topsoe, N. Y., Pedersen, K. and Derouane (1981). Infrared Temperature Programmed Desorption Study of the Acidic Properties of ZSM-5 Type Zeolites. J. of Cat. 70; 41- 52

Y. S., Prasad and N. N., Bakhshi, J. F., Mathews and R. L., Eager (1986a). Catalytic Conversion of Canola Oil to Fuels and Chemical Feedstocks. Part 1: Effect of Process Conditions of the Performance of HZSM-5 Catalyst. Can. J. Chem Eng. 64: 278-284

Y. S., Prasad and N. N., Bakhshi, J. F., Mathews and R. L., Eager (1986b). Catalytic Conversion of Canola Oil to Fuels and Chemical Feedstocks. Part II: Effect of Co-Feeding Steam on the Performance of HZSM-5 Catalyst. Can. J. Chem Eng. 64: 285-296

Van Mao, L. R., Le, T. S., Fairbairn, M., Muntasar, A., Xiao, S. and Denes, G., (1999) ZSM-5 Zeolite With Enhanced Acidic Properties, Applied Catalysis A: General, 185, 41-52